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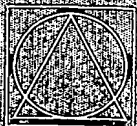
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Line Reum

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Fremgangsmåte for økt oljeutvinning

The field of the invention

The present invention regards the use of natural gas in the development of industry and oil fields. In particular, the invention regards a method and a plant for integrated production of synthesis gas for synthesis of higher hydrocarbons or oxygenated

5 hydrocarbons and gas for injection into an oil reservoir.

The background of the invention

Injection of various gases into an oil reservoir in order to enhance the oil recovery from the reservoir, and to stabilize it, has long been known and used. Gases such as CO_2, N_2

10 and natural gas will reduce the surface tension between gas and oil, and thus contribute to both increased recovery and stabilization of the reservoir.

During enhanced oil recovery operations, a number of techniques are applied that depend on the nature of the specific field and wells, their maturity, seasonal variations

15 etc. The most common approaches are secondary oil depletion using water flooding or gas injection. Further alternatives, often referred to as tertiary depletion, include injection of gas after water, alternating gas and water injection (WAG), and simultaneous water and gas injection (SWAG). Thermal treatment by injection of steam or in situ combustion is also possible. By gas we here mean all viable options like

20 methane, other hydrocarbons, nitrogen, air, flue gas, carbon dioxide or mixtures of any of these gases.

Natural gas as such may be injected into fields where the gas does not have a net value that exceeds the excess profits of increasing the oil recovery in the field.

25

An oil field contains hydrocarbon liquids (oil), associated gas and water.

Cleaning waste gas from the combustion on the production installation can provide CO_2 for injection into oil reservoirs. In addition it has been suggested that CO_2 cleaned from

30 the waste gas from gas power plants be re-injected by laying a pipeline from a gas power plant to the production installation for hydrocarbons.

N_2 may be produced together with O_2 in a so-called air separation unit (ASU). In an oil field, such an air separation unit will normally produce N_2 with a purity of >99.9% and oxygen-enriched air. There is little or no need for this oxygen-enriched air on the oil field, and all or most of this is therefore released.

5

Separation of air into an "oxygen-depleted stream" and an "oxygen-enriched stream" is described in US 5,388,645 and US 6,119,778. The oxygen-depleted stream is used for injection into a "solid carbonaceous formation" for improved recovery of methane and at least a part of the oxygen-enriched stream is used for reaction with a reactant stream

10   containing at least one oxidizable reactant. Examples of processes are steel making operations, production of non-ferrous metals, chemical oxidation processes and production of synthesis gas for Fischer-Tropsch synthesis of higher from natural gas. The oxygen-depleted stream has a nitrogen to oxygen volume ratio of 9:1 to 99:1. A too high ration may lead to the formation of an explosive gas. An oxygen-depleted gas, e.g.

15   nitrogen, for injection into an oil field to enhance the production preferably includes less than 0.1 % oxygen.

No other integration between the processes using the oxygen-depleted and oxygen-enriched streams is mentioned in US 5,388,645 or US 6,119,778.

20

US 4,344,486 relates to a method for enhanced oil recovery where a mixture of carbon dioxide and contaminants comprising hydrocarbon, hydrogen sulfide or mixtures thereof is recovered from an underground formation; the recovered mixture is combusted with an oxygen enriched stream to form concentrated carbon dioxide stream

25   where at least a part of said carbon dioxide stream is injected into a underground formation to enhance recovery of liquid hydrocarbon. It is also described to use nitrogen from an air separation unit for injection together with the concentrated carbon dioxide stream.

30   Natural gas may also be used as feed for a number of processes such as the production of methanol, di-methyl ether or other oxygenated hydrocarbons, and/or synthetic

fuel/propellant. This can take place in accordance with known processes such as described in PCT/NO00/00404.

Plants for production of methanol and other oxygenated hydrocarbons and/or synthetic fuel often require O_2 produced in an air separation unit in order to produce synthesis gas
5 ("syngas"). Syngas is a mixture of CO, CO_2, H_2 and water vapor and some non-reacted natural gas. The syngas is used in various synthesis reactions, such as for the production of methanol and other oxygenated hydrocarbons, heavier hydrocarbons and ammonia. The oxygen produced in an air separation unit in such a plant is typically >95% pure oxygen, while the nitrogen will be relatively impure nitrogen that is not suitable for
10 other applications, and is therefore released to the atmosphere.

A process for preparation of higher hydrocarbons and for enhancing the production of crude oil from an underground formation is described in CA 1,250,863. The off-gas from the synthesis plant is oxidized into mainly CO_2 and H_2O before it is injected into the underground formation. Preferable the presence of nitrogen is avoided by using
15 oxygen from an air separation unit for all oxygen-demanding processes.

A summary of the invention
According to the present invention, there is provided a method for increasing oil recovery from an oil reservoir in which method gas is injected into the reservoir,
20 comprising the steps of:
- separation of air into an oxygen-rich fraction and a nitrogen-rich fraction,
- providing a natural gas stream and leading the natural gas stream and at least a part of the oxygen-rich fraction to a reformer for conversion to synthesis gas mainly comprising H_2, CO, CO_2 and lower amounts of non-converted methane,
25 water vapor and nitrogen,
- formation of methanol or other oxygenated hydrocarbons or higher hydrocarbons from the synthesis gas in a synthesis unit,
- withdrawing raw synthesis products and a waste gas from the synthesis unit, and
- injecting the nitrogen-rich fraction and at least a part of the waste gas into the oil
30 reservoir to increase the oil recovery from the reservoir,

4

Preferably all or some of the waste gas from the synthesis unit is sent to a CO2 recovery unit including a CO shift converter where CO2 is removed and injected into the reservoir and the remaining hydrogen-rich stream is used for other purposes.

5   It is preferred that steam or water generated during the syngas production and/or synthesis is injected into the reservoir.

Also provided is a plant for providing gas for downhole injection for pressure support in an oil reservoir for recovering of hydrocarbons and production of oxygenated

10   hydrocarbons or higher hydrocarbons from natural gas, comprising:
— an air separation unit for production of an oxygen-rich fraction for supply to processes that require oxygen, and a nitrogen-rich fraction for injection;
— a reformer for conversion of a mixture of natural gas, water and oxygen or oxygen enriched air from the air separation unit into a synthesis gas comprising mainly H_2,

15   CO, CO_2 and small amounts of methane in addition to any inert gas, such as nitrogen;
— a synthesis unit for conversion of the synthesis gas for synthesis of oxygenated hydrocarbons, or for synthesis of higher hydrocarbons;
— means for injecting gas into the reservoir;

20   — means for transferring nitrogen from the air separation unit to the means for injecting gas; and
— means for transferring at least a part of a waste gas from the synthesis unit to the means for injecting gas.

25   Preferably the plant additionally comprises a tail gas treatment unit for removing CO by a shift reaction and separation of hydrogen from the remaining tail gas.

It is also preferred that the plant comprises means for transferring the remaining tail gas from the tail gas treatment unit to the means for injecting gas.

30

The synthesis unit preferably comprises one or more once-through Fischer-Tropsch units for synthesis of higher hydrocarbons.

It is preferred that the plant comprises means for introducing all or parts of the separated hydrogen from the tail gas treatment unit into the Fischer-Tropsch loop to adjust the H_2/CO ratio to a desired level.

5

By combining a plant for production of high-purity nitrogen with the production of oxygen, the co-producing air separation unit only becomes 10-20 % more expensive than an air separation unit that only produces high-purity nitrogen for injection into oil fields. This allows significant cost savings, both for production of synthesis products such as methanol and synthetic fuel, and for oil field injection.

10

Additionally, several of these EOR injection fluids or gases are or can be produced as part of the operation of a GTL plant. The possibilities are at least:

15 - Nitrogen from the ASU unit, as described in detail in this application.
    - Flue gas, particularly if traditional SMR (steam methane reforming) is used in whole or partly.
    - Water produced by the Fischer-Tropsch process.
    - Steam produced by the FT-process.
20 - Light hydrocarbons, including methane, produced by the FT-process.
    - CO2 produced by the syngas process, also described in detail in this application.

More detailed utilization of some of these possibilities can be illustrated by the examples below. It should be recognized that there are multiple ways to combine the
25 described injection gases, both by mixing with natural gas, and by applying intermittent operation, also using water part of the time.

A brief description of the figures
30 Figure 1 shows a schematic diagram of an embodiment of the present invention;
Figure 2 shows a schematic diagram of alternative options for the present invention;
Figure 3 shows an alternative embodiment of the present invention;

Figure 4; shows an alternative embodiment of the present invention; and

Figure 5 is an illustration of the economical impact of the integrated process according to the present invention.

5   **Detailed description of the invention**

Figure 1 is a schematic diagram showing the principal features of a preferred embodiment of the present invention. Air is drawn in through an air intake 1 to an air separation unit 2, where it is separated into the main components nitrogen and oxygen. The air separation unit differs from traditional air separation units used for production

10   of oxygen to reformers or for production of nitrogen for injection into an oil well, in that it produces both nitrogen and oxygen with a high purity. The produced nitrogen typically has a purity of >99.9%, while the oxygen typically has a purity of 98 – 99.5%.

The nitrogen is passed through line 3 to a compressor 4 where it is compressed to the

15   desired pressure, e.g. of the order of 50 - 400 bar. From the compressor 4, the compressed nitrogen stream is passed through a line 5 to a plant 6 for injection of gas into a field, a so-called EOR unit ("Enhanced Oil Recovery").

The oxygen is passed through a line 7 to a synthesis gas production unit, a so-called

20   reformer 8.

Natural gas is fed to the plant through a gas inlet 9. Prior to the natural gas being sent into line 11 to the reformer for production of synthesis gas, it is treated in a pre-treatment unit 10 in which sulfur compounds are removed in a conventional manner.

25   Steam is then saturated into the gas and/or added directly to the gas. The saturation may take place by means of a so-called saturator. Often, the gas is also treated in a so-called pre-reformer in order to convert all heavier hydrocarbons (C2+) to methane, CO and CO2 before the gas is sent into the reformer 8.

30   In the reformer, the following are the main chemical reactions to take place during the production of synthesis gas:

1. $CH_4 + H_2O = CO + 3H_2$, steam reforming
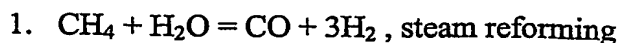
2. $CH_4 + 3/2\ O_2 = CO + 2\ H_2O$, partial oxidation

3. $CO + H_2O = CO_2 + H_2$, shift reaction

Reaction 1 in the reforming reactor is highly endothermic, and the heat required for the
5   reaction may either be added through external heating, such as in a steam reformer, or
through a combination with internal partial oxidation according to reaction 2, such as in
an autothermal reformer.

In a steam reformer (SR), natural gas (NG) is converted in a tubular reactor at a high
10   temperature and relatively low pressure. A conventional steam reformer consists of a
large number of reactor tubes in a combustion chamber. Conventional steam reformers
are operated in a pressure range from approximately 15 to 40 bar. The outlet
temperature for such a reformer can get up to 950 °C. The heat required to drive the
reaction is added by means of external heating in the combustion chamber in which the
15   reformer tubes are installed.

The reformer may be top, bottom or terrace fired. The heat can also be transferred to the
reaction by means of convective heat as in a heat exchanger reactor. The ratio between
steam and carbon in the feed gas is from 1.6 to 4. The composition of the synthesis gas
20   may as an example be expressed in stoichiometric numbers ($SN=(H_2-CO_2)/(CO_2+CO)$).
The stoichiometric number for the product stream from the steam reformer is
approximately 3 when the natural gas contains pure methane. A typical synthesis gas
from a conventional steam reformer contains approximately 3-volume % methane on
dry gas basis.
25

In an autothermal reformer (ATR), the synthesis gas production mainly takes place
through reactions 1 and 2, such that the heat required for reaction 1 is generated
internally via reaction 2. In an ATR, natural gas (methane) is led into a combustion
chamber together with an oxygen-containing gas such as air. The temperature of the
30   combustion chamber can get up to over 2000 °C. After the combustion, the reactions are
brought to an equilibrium across a catalyst before the gases leave the reformer at a
temperature of approximately 1000 °C. The stoichiometric number, SN, for the product

stream from an ATR is approximately 1.6 – 1.8. The pressure may typically be around 30-40 bar, but a significantly higher pressure has also been proposed, such as in the range of 40 – 120 bar. The steam/carbon ratio may vary with the intended application, from 0.2 to 2.5.

5

An alternative autothermal reformer makes use of a concept called partial oxidation (POX). Such a reformer does not contain any catalyst for accelerating the reactions, and will therefore generally have a higher outlet temperature than an ATR.

10   Natural gas reforming may also take place through combined reforming (CR), where the reformer section consists of a SR and an ATR. A combination of SR and ATR allows the composition exiting the reformer section to be adjusted by regulating the duties of the two reformers. SR will in CR be operated under somewhat milder conditions than in the case of normal SR, i.e. at a lower temperature. This results in a higher methane

15   slippage in the outlet gas from the reformer. This methane content is converted in the subsequent ATR. The ratio between steam and carbon in the gas feed will, for such a reformer, lie in the range 1.2 to 2.4, with a stoichiometric number, SN, of around 2 or slightly on the high side of 2.

20   The desired composition of the synthesis gas will depend on the process for which it is to form the raw material. The optimum stoichiometric number for methanol synthesis s around 2.05, while the desired stoichiometric number for production of synthetic fuel often lies in the range 1.6 to 1.9, as a higher stoichiometric number gives a greater yield of lighter hydrocarbons than desirable.

25

After reforming, the synthesis gas is cooled by being heat exchanged with water to give steam. Upon further cooling, water is condensed and separated from the synthesis gas before the synthesis gas is sent via a line 12 to a synthesis unit 15.

30   The synthesis unit 15 may for instance be a synthesis unit for production of synthetic fuel (heavier hydrocarbons), comprising a so-called Fischer-Tropsch reactor (F-T

reactor), or a synthesis unit for production of oxygenated hydrocarbons such as methanol and di-methyl ether.

5   When the synthesis unit 15 is a synthesis unit for production of synthetic fuel, the reaction may be described using the following reaction equation:

$$nCO + 2nH_2 = [-CH_2-]_n + nH_2O$$
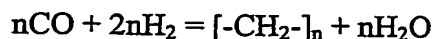
The reaction is highly exothermic. The Fischer-Tropsch synthesis is well known and is described e.g. in PCT/NO00/00404.

10   When the synthesis unit 15 is a synthesis unit for production of methanol, this synthesis takes place according to the following two reaction equations:

$$CO + 2H_2 = CH_3OH$$
$$CO_2 + 3H_2 = CH_3OH + H_2O$$
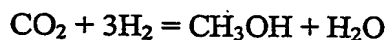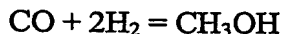
These exothermal reactions normally take place in a tubular reactor at a pressure of 60-
15   100 bar and a temperature of 230-270 degrees C. The methanol synthesis is also well known and is described e.g. in PCT/NO00/00450.

Both of the above synthesis units comprise a number of components *per se*, and both processes normally include internal recycling of non-reacted synthesis gas in order to
20   increase the carbon efficiency of the process.

The product from the synthesis unit 15 is extracted through a product outlet 16 for further treatment. Non-reacted synthesis gas and inert gas that collects in the loop can be removed from the synthesis unit 15 through line 17. This gas will in the following
25. description be denoted the waste gas from the synthesis unit. The amount and composition of the waste gas from the synthesis unit depends on the released methane in the synthesis gas from the reformer section, as well as selected process parameters in the synthesis unit.

30   For the methanol synthesis, the volume of waste gas from the synthesis unit may be small. In this case, this gas may be released or combusted prior to being released in order to avoid emissions of hydrocarbons and CO.

If CO_2 is required for injection into the oil well in addition to nitrogen, or if environmental conditions require the emission of CO_2 from the plant to be reduced, the waste gas from the synthesis unit may alternatively be further passed to a CO shift

5 converter 18 in which non-converted CO is converted according to the following reaction equation:

$$CO + H_2O \rightarrow CO_2 + H_2$$
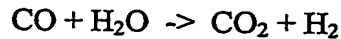
in order to make it easier to separate out the carbon contents of the gas.

10 From the CO shift converter, the gas may if required be led through a line 19 to a CO_2 recovery unit 20 in which CO_2 is separated from the other constituents of the gas. CO_2 may be separated out by means of an absorption process, e.g. by means of an amine, a cryogenic process or possibly by means of membranes. From the recovery unit 20, CO_2 is led via a line 21, a compressor 28 and further via a line 29 to EOR unit 6.

15

The gas that was separated from CO_2 in the recovery unit 20, and which mainly consists of H_2, CH_4 and inert gases, is passed further through a line 22 to other uses in a unit 23. The unit 23 may be a furnace in which the gas is combusted under the addition of air, oxygen or oxygen-enriched air and provides heat for a heat-requiring process.

20 Alternatively, the gas may be burnt in a gas turbine alone or as additional heating. Alternatively, hydrogen may be separated from the gas before it is burnt or alternatively released. Hydrogen may here be used for hydrogen-requiring processes such as e.g. upgrading of oil by sweetening (removal of sulfur), for saturation of unsaturated hydrocarbons and hydrocracking or for use in fuel cells.

25

If there is a great need for CO_2 for injection, the use of a so-called "once through" reactor in the synthesis unit 15 may also be envisaged, i.e. a reactor without any recycling.

30 Figure 2 shows alternative and optional embodiments of a plant according to the present invention. The figure is based on the same principal units as Figure 1, but some optional, and in some cases preferred, additional units besides bypass lines and

feedback lines, have been added in order to ensure the highest possible conversion or in order to adjust the composition of the gas.

5 A CO_2 recovery unit 13 may be interposed between the reformer 8 and the synthesis unit 15. By so doing, a desired amount of CO_2 can be removed from the synthesis gas and passed through a line 27 to the compressor 28, where it is brought together with CO_2 from line 21. This can be used as a means of changing the stoichiometric number of the synthesis gas so as to give it an optimum composition.

10 When the synthesis unit 15 is a synthesis unit for production of synthetic fuel, synfuel, it may also be desirable to recycle non-reacted synthesis gas from line 17 to the reformer via line 26. By recycling via line 26, the H_2/CO ratio of the synthesis gas may be adjusted to the desired value, i.e. around 2.0 or just below 2.0, and the CO yield and thereby also synthetic fuel yield may be increased by the high content of CO_2 in the 15 recycling gas suppressing further conversion of CO to CO_2 through the shift reaction in the autothermal reformer. Here, it should be noted that CO_2 is to be considered as an inert gas in the F-T synthesis.

If the reformer produces more synthesis gas than can be converted in the synthesis unit, 20 some of the synthesis gas may be led from a line 14 running between the CO_2 recovery unit 13 and the synthesis unit 15, and around the synthesis unit in a bypass line 25. This may also be desirable if there is a wish to produce more heat or power in a furnace or gas turbine 23.

25 In certain cases it may also be desirable to remove a volume of nitrogen from line 5 out into a line 24 and bring this together with the gas in line 22, which is led to a gas turbine in unit 23 in order to control the combustion and generation of heat in this.

The units 13 and 20 for separating CO_2 from the remainder of the gas are known units. 30 By the reformer 8 being supplied with pure oxygen instead of air, the volume of gas to be treated becomes considerably smaller. The separation in the units 13, 20 may take

place in a known manner by means of semi-permeable membranes or by absorption with subsequent desorption, e.g. in an amine solution.

The air separation unit 2 is preferably a plant based on cryogenic distillation, however it is also possible to use plants based on pressure swing adsorption or membranes or a combination of these technologies.

Figure 3 shows a third embodiment in which non-converted synthesis gas from the synthesis unit 15 is combusted with pure oxygen in a furnace or gas turbine 30. Units having the same reference numbers as in Figure 1 or 2 indicate similar units with a similar functionality.

Oxygen is passed from line 7 through a line 40 and mixed with CO_2 in a line 41, from where it passes into furnace or gas turbine 30. The waste gas from the furnace or gas turbine 30 goes via a line 31 to a catalytic secondary combustion chamber 32 in which the remaining fuel in the form of CO, H_2 or non-combusted hydrocarbon is converted catalytically. The products of combustion from the secondary combustion chamber 32 containing water and CO2 are passed via a line 33 to a condensation unit 34, where water is condensed out and led out through a line 35, while CO_2 is passed to the EOR unit 6 via a line 36.

CO_2 may be led from line 36 via a line 37 to a compressor 38. For this configuration, some compressed CO_2 must be recycled via line 41 to the furnace or gas turbine 30 in order to maintain the combustion temperature in this below a given maximum temperature.

If the requirement for heat and/or power is great, or there is a requirement for large volumes of CO_2, natural gas from line 11 may be led via a line 42 directly to the furnace or gas turbine 30.

Preferably, the combustion in the furnace or gas turbine 30 takes place at an elevated pressure, such as from 2 to 100 bar, more preferably from 20 to 40 bar. Having the

combustion take place with pressurized oxygen facilitates the separation of CO_2 in the following condensation unit 34.

Figure 4 illustrates a fourth embodiment of the present invention wherein the synthesis

5   unit is a once-through Fischer-Tropsch system for synthesis of higher hydrocarbons from natural gas. Units having the same reference numbers as in figure 1, 2 and/or 3 indicate units having the same functionality.

Natural gas from the gas inlet 9 is saturated and pre-reformed in the pre-treatment unit

10   10. Steam for the pre-treatment is added through a steam line 50. The pre-treated natural gas is passed from the pre-treatment unit 10 to the reformer 8, for production of syngas, through line 11. Oxygen from the air separation unit (ASU) 2 is introduced into the reformer 8 through line 7. Nitrogen from the ASU 2 is passed through line 3 to the plant for injection (EOR) 6.

15

The reformer 8 is a traditional steam methane reformer (SMR) or an autothermal reformer (ATR) and may include one or more units for syngas production and/or separation of the produced syngas. Syngas produced in the reformer 8 is passed through line 12 to a syngas cool-down unit 52. All or a part of the flue gas from the reformer 8,

20   mainly comprising CO_2 and H_2O, may be separated from the syngas and led to the EOR 6 through a line 51. The line 51 is dotted to indicate that the line 51 is not obligatory. If the reformer 8 is a ATR unit there will be no flue gas and no line 51.

In the syngas cool-down unit 52, water is introduced through line 53 and steam is

25   withdrawn through a line 54. The steam in line 54 may be led to the EOR for injection into the oil reservoir. If some or all of the steam in line 54 is not needed for injection, some or all of the steam in line 54 may be used for other purposes. Some of the steam may be transferred to line 50 and be introduced to the pre-treatment unit 10. Alternatively, the steam may be utilized in a not shown turbine to generate power for

30   other uses.

The cooled down syngas leaves the cool-down unit 52 through a line 42 and is passed through a membrane unit 43 where hydrogen is separated from the syngas to give a H_2/CO ratio that is useful for the further reactions. A not shown water separation unit placed between the cool-down unit 52 and the membrane unit 43 to separate water form

5   the syngas before it is introduced into the membrane unit 43.

The decant water separated from the syngas is led through line 49 to the EOR 6 and hydrogen is withdrawn through line 48 and can be used as fuel gas or for feed gas desulfurisation or hydrotreating/hydrocracking of oils fractions. The syngas leaving the

10   membrane unit 43 through a line 44 is introduced into a Fischer-Tropsch (FT) synthesis loop 56 for production for higher hydrocarbons. Higher hydrocarbons in the present description are hydrocarbon molecules having three or more carbon atoms, more preferably five or more carbon atoms.

15   Further background on FT synthesis may be found in WO/01/42175 to Statoil ASA, and the prior art cited therein.

Raw higher hydrocarbon product from the FT synthesis loop 56 is withdraw through a line 57 and the produced water is withdrawn through a line 58 and passed to the EOR 6.

20

The remaining gas (tail gas) mainly comprising CO_2, lower hydrocarbons, H_2O, CO and some nitrogen, is withdrawn through a line 62.

The tail gas in line 62 is introduced to a tail gas treatment unit 63, in which CO is

25   removed by a shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$). The remaining tail gas is split into a hydrogen rich stream that is withdrawn through a line 64, and a hydrogen poor fraction that is withdrawn through a line 65. The hydrogen in line 64 may be used for other reactions requiring hydrogen and/or be introduced into the Fischer-Tropsch loop 56 to adjust the H_2/CO-ratio in the syngas.

30   The remaining tail gas, or the hydrogen poor fraction, in line 65 may be split into two streams, one in a line 59 that is introduced to the EOR and another stream in a line 45

that is used as fuel for a power generation unit 46. The tailgas introduced into the power generation unit 46 is burned in presence of air or oxygen enriched air to produce power or heat. Flue gas from the power generation unit 46 is led through a line 47 to the EOR 6 for injection.

5

The great advantage of the present method and plant is that they allow simple and energy efficient operation of the combined plant. The present method also allows a more efficient and financially justifiable method of removing CO_2 from the waste gas from a methanol plant or plant for production of synthetic fuel, for injection, so as to

10   allow the emission of CO_2 to be eliminated or at least reduced considerably.

The present invention in its different embodiments, also makes it possible to customize the plant respectively alter the working conditions according to the specific need and / or variations in economical and technical factors. Some advantages by using the

15   embodiment according to figure 4 are listed below:

-    Water injection.

Water or steam are generated several places in the GTL plant. First it should be recognized that steam is generated at elevated pressures and temperatures. In particular, the elevated pressure will be an advantage for EOR, as work for

20   compression to the desired injection pressure will be reduced. Often the energy content of the steam is utilized in a steam turbine to produce electricity or for heat input to process units like distillation towers, whereby the steam may be condensed to water.

25   Water/steam is produced (synthesized) only in the FT reactor by the reaction:

$$nCO + 2nH_2 \longrightarrow nH_2O + (-CH_2-)_n$$
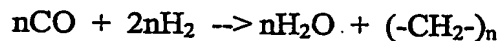
In other words, water or steam is synthesized in the same amount on a molar basis

30   as the number of $-CH_2-$ units in the hydrocarbon product. This will be ca. double the amount of oxygen (mole) produced by the ASU, or half the amount of nitrogen (excluding oxygen loss to CO_2 in the calculation). It should also be

understood that there is a significant use of boiler feed water for steam generation in a FT-plant, notably in the heat exchanger for the FT-reactors themselves and to cool down the synthesis gas. Furthermore, there is also a significant use of cooling water in a F-T plant.

5

The water generated in the FT reaction will unavoidably contain small amounts of impurities comprising alcohols, acids and other oxygenates that often will have to be removed in costly water treatment facilities, before disposal. This purification may not be necessary if the water is used for EOR.

10

- Steam injection

As described in Example A, steam is generated several places in the GTL plant. As such, this is a valuable product that at least partly may be used to produce electric power. Particularly in a remote location there may be more feasible to use

15   steam for EOR.

All in all, when water or steam is used for EOR, integration with a GTL plant can also have the following benefits:
- Water may not be available from other sources.

20   - Water and/or steam are available at an elevated pressure.
- Steam is available (high pressure and temperature).
- Purification of the produced water is avoided.

- Flue gas injection

25   Flue gas may essentially come from two sources, either the exhaust gas from a gas turbine or a fired heater integrated with the GTL facility, or from application of a steam reformer (SMR) for production of synthesis gas (in this application also called waste gas). If flue gas is desirable for EOR, this may give an advantage for SMR (steam methane reforming) over other syngas technologies like ATR

30   (autothermal reforming) or GHR (gas heated reforming). SMR may also be part of the total syngas generation option, like in combined reforming or tail gas

reforming.

- Injection of FT-tail gas.

Unless the intention of the EOR operation is simple gravity stabilization, that is gas compression from top to bottom of the oil reservoir, it frequently is an advantage if the gas has a high miscibility with the oil. Nitrogen has low miscibility, methane somewhat higher, whereas CO2 and higher hydrocarbons (C2+) are more easily mixed with the oil.

It is well known that optimization of an GTL-plant will comprise recycle streams, e.g. recycle of the tail-gas (light off-gas) from the FT-reactor to the syngas unit or back to the FT-reactor, in order to increase overall energy and carbon efficiency. This tail gas from the FT-reactor, usually after separation of the main products (C5+) and water, then will contain CO2, light hydrocarbons, and unconverted syngas. Whole or part of the tail gas can be used for EOR, possibly after mixing it with nitrogen, natural gas or CO2 from a dedicated CO2 separation unit. Now it may be a disadvantage, particularly for moderate conversion in the FT-reactor, that the tail gas contains unconverted syngas. One option therefore is to pass the gas through an additional syngas conversion unit, like a second FT-reactor, to secure high conversion before EOR. Hydrogen may also be removed in a dedicated unit, for instance a polymer membrane separator, and CO converted to CO2 and hydrogen in a shift reactor.

Using the Fischer-Tropsch tail gas for EOR opens up for a significant simplification and cost reduction for the GTL plant. In fact, a once-through concept might be feasible. No recycle also opens up for a simplified ASU using only enriched air for an ATR syngas generator. This enriched air may contain 25 % nitrogen that will end up in the tail gas and thereby the EOR stream.

Those skilled in the art will appreciate that there may be units in the above figures for adjusting the pressure of the gases, such as compressors or reducing valves that are not shown, but which are necessary in order to match the pressures of the various units and

to ensure that the streams flow in the right direction. Moreover, there may be units for heating or cooling, or heat exchangers that are not shown here, the function of which is to optimize the energy efficiency of the plant.

5   In must be understood that for off-shore oil or gas fields, one or all the processing units described in this application, also can be placed off-shore, like the entire GTL-plant or only the ASU or the syngas section.

Example 1

10   Calculations have been carried out for a plant according to Figure 1 for production of methanol, which in addition comprises a bypass line that leads some of the synthesis gas in line 12 past the synthesis unit 15 and on to line 17.

The air separation unit can deliver 38 400 MTPD N_2 and 6400 MTPD O_2. This air

15   separation unit requires approximately 115 MW of power, which is delivered in the form of high-pressure steam from the synthesis gas section.

The nitrogen is extracted at 3 bar and 0 degrees C. The gas is compressed to 220 bar for injection. Compression requires approximately 304 MW.

20

The oxygen can be fed to an autothermal reformer for production of synthesis gas from natural gas. The process operates with a steam/carbon ratio of 0.6. The temperature and pressure at the outlet from the ATR is 1030 degrees Celsius and 45 bar respectively. See Table 1 for the natural gas composition. Note! All compositions are given on a dry

25   basis, i.e. without water.

	Natural gas Mole %	Oxygen Mole %
CH_4	83.7	
C_2H_6	5.2	
C_{3+}	3.2	
CO_2	5.2	
$N_2 + Ar$	2.7	1.0
O_2	0.0	99.0

H₂O	0.0	
Sum	100	'
Total [Sm³/hr]	367 000	190 850

Table 1.   Composition of feeds to synthesis gas section

Synthesis gas is compressed to 90 bar and mixed with recycled hydrogen in order to

5   achieve a stoichiometric number of 2.56 prior to the methanol synthesis. 10 000 MTPD

of methanol is produced.

	ATR outlet	MeOH reactor inlet	Purge gas	CO shift converted purge gas	CO$_2$ purified purge gas
	Mole %	Mole %	Mole %	Mole %	Mole %
H$_2$	62.9	65.9	27.3	38.7	52.6
CO	28.5	16.3	24.2	3.1	4.2
CO$_2$	4.8	6.7	12.7	26.8	0.4
CH$_4$	2.5	7.2	23.7	21.6	29.4
N$_2$ + Ar	1.3	3.9	12.1	9.8	13.4
Sum	100	100	100	100	100
Total [Sm^3/hr]	1 093 000	3 488 000	113 000	136 000	100 000

Table 2. Gas compositions

The waste gas from the synthesis unit, the purge gas, is sent to CO shift conversion. 35
t/h of steam is added in order to convert 85% of CO to CO$_2$ in a low temperature shift
converter (200 degrees Celsius).

99% of the CO$_2$ in converted purge gas (equivalent to 1700 MTPD CO$_2$) is recovered in
an MDEA process. Due to a high concentration of CO$_2$ in the natural gas feed, this
example includes CO$_2$ removal prior to ATR (equivalent to 800 MTPD CO$_2$), so that the syngas has
total amount of recovered CO$_2$ is 2500 MTPD. Recovered CO$_2$ is compressed to 220
bar, and may if so desired be mixed with nitrogen prior to injection into the reservoir.
CO$_2$ will then constitute around 6.2 weight % of the total injection gas. CO$_2$ constitutes
a relatively small share of the total injectable gas. The cleaning of this may end up being
so costly that it will only be done if required by the authorities.

The remaining purge gas is used in fired heaters for superheating of steam in power
production and preheating of natural gas feeds.

Power balance	[MW]
ASU incl. O$_2$ compression	115
CO$_2$ recovery	3
CO$_2$ compression	11
N$_2$ compression	304
Synthesis/methanol section	-155
Total	278

Table 3. Power balance

Here, the requirement for added power is approximately 280 MW.

Example 2

A simulation on a plant as illustrated in figure 4 was performed. 367 000 Sm^3/hr natural

5   gas from line 9 was mixed with 183 t/h steam from line 50 in order to reach steam to

carbon ratio of 0.6. The mixture was preheated to 600°C and fed to an auto-thermal

reformer (ATR) 8. 275 t/hr oxygen (6600 MTPD) was introduced into the ATR 8 from

the line 7. The outlet temperature from the ATR 8 was 1030°C. The amount of oxygen

consumed in the ATR corresponds to a co-production of N$_2$ of 39600 MTPD.

10

The syngas leaving the ATR 8 through line 12, which is in equilibrium and at a

temperature of around 1030°C, is cooled to about 350°C with evaporating water in the

syngas cool down unit 52 producing about 830 t/h saturated 110 bar steam that is

withdrawn in line 54. The steam in line 54 may be utilized for EOR as illustrated in

15   figure 4, or in turbines to generate power.

After the syngas has been cooled down 178 t/h decant water is removed and about 60

000 Sm^3/hr hydrogen (hydrogen purity of 90%) is separated in the membrane unit 43

before the syngas is fed to the Fischer-Tropsch loop 56. The decant water is withdrawn

20.   through line 49 and may be used for EOR. The separated hydrogen is withdrawn

through line 48 and is introduced into line 64 or is being used for any process, either

connected to the plant in question or another plant requiring hydrogen.

The Fischer-Tropsch loop produces 233 t/h gas that is withdrawn through line 65, 138

25   t/h syncrude (long paraffin chains) that is withdrawn through line 57 and 198 t/h water

that is withdrawn through line 58.

The syncrude must be further processed in a way known by the skilled man in the art,

by a not shown hydrotreater, hydrocracker and/or solvent de-waxing unit in order to

30   give desired products (LPG, naphtha, diesel and/or lube oils).

The water from the Fischer-Tropsch loop that is withdrawn in line 58, contains dissolved impurities (mainly alcohols) and may be transferred to the EOR 6 and be injected into the oil field.

5   To maximize the amount of CO_2 available for recovery from the gas in line 65, the gas may be shifted with a low-temperature copper catalyst to convert about 86% of the CO into CO_2. A CO_2 recovery of 95% will then imply that 180 t/hr CO_2 is available for EOR purpose from the gas in line 65. The composition of the gas in line 65 is given in Table 4.

10

Component	mole %
H_2	40
CO	2
CO_2	39
N_2	4
CH_4	11
Others	4

Table 4.   Composition of the gas in line 65

After the CO_2 recovery, there will still be about 830 MW heat available (LHV).

15   The gas compositions of some key streams are shown in Table 5.

Line	Number	9	12	48	42
	Description	NG Feed	Syngas	Hydrogen	FT Feed
Total Stream Properties					
Rate	KG-MOL/HR	15521,3	56424,8	2566,3	43977,4
	KG/HR	301848,2	761722,8	13377,3	570334,8
Composition					
Component Molar Rate	KG-MOL/HR				
	H2	0,000	0,514	0,906	0,606
	CO	0,000	0,238	0,033	0,304
	CO2	0,052	0,049	0,052	0,059
	H2O	0,000	0,178	0,006	0,004
	N2	0,027	0,007	0,001	0,009
	METHANE	0,837	0,013	0,001	0,017
	ETHANE	0,052	0,000	0,000	0,000
	PROPANE	0,032	0,000	0,000	0,000

Table 5: Composition in key process gas lines

Model for evaluation of economical value

The benefit of using the nitrogen byproduct produced by the air-separation unit (ASU) of a GTL plant, for enhanced oil recovery (EOR), may be evaluated by analyzing the potential impact on the gas price of the GTL plant. The natural gas price is without any doubt a major factor determining the profitability of such a plant, and a credit will be achieved for selling nitrogen.

Nitrogen and methane has roughly the same properties in EOR operations, essentially as pressure support. In the outset, we may therefore assume that the value of the neat nitrogen is equivalent to the gas price. We then will have:

P: Natural gas price in the area of the GTL facility.

$$P^{Net}(GTL) = aP - bcP \quad \text{(Area gas price – credit for nitrogen sale)}$$

where the coefficients are:

a) A factor reflecting the impact on the general gas price in the area due to the integration. If P is the gas price with independent GTL and EOR operations, integration will significantly decrease the total demand for gas, and may therefore put pressure on the price, i.e., $a < 1$.

b) The amount of nitrogen produced for a given amount (moles or energy) of natural gas used by the GTL plant. For a facility with an ATR (autothermal reformer) unit, a typical oxygen consumption O2/NG is 0.63, giving N2/NG = 2.34. This number will vary with the technical concept, gas composition etc., but is used in the following to illustrate the impact of the EOR-GTL integration.

c) A factor presumably < 1 taking into account that all the nitrogen produced may not be sold, e.g. due to overall well management, maintenance etc. Further, operational risks regarding continuous nitrogen delivery may put pressure on the nitrogen price.

The equation above may be modified further:

$$P^{Net}(GTL) = aP - bcP + I + dS$$

where

I: The investment needed to implement the integration. This will essentially be some additional cost in the ASU to secure production of nitrogen at a required purity, (additional) compression of the nitrogen, piping from the GTL to the EOR plant

5   and possibly credit for energy integration. All these factors are recalculated by accepted methods to a cost (e.g. net present value) per amount natural gas used in the GTL plant.

S: Total savings (per amount natural gas) in the GTL gas price by the integration. This

10   means that

$$S = P - (aP - bcP + I)$$

d: The part of the savings that is passed onto the EOR operator for participating in the

15   integration project, usually $0 < d < 0.5$. The factor d might be a complicated function and there might also be overlap between the impact of factors c and d.

Illustrating example:

Assuming that a=1, b=2.34, c=1, I=0.2 (here 0.2 USD/MMbtu) and d=0.5, the impact of

20   the integration is illustrated in Figure 5. The lines are:

I: $P^{Net}(GTL) = aP$ $= P$ (No EOR)
II: $P^{Net}(GTL) = aP - bcP$ $= -1.34P$
III: $P^{Net}(GTL) = aP - bcP + I$ $= -1.34P + 0.2$
IV: $P^{Net}(GTL) = aP - bcP + I + dS$ $= -0.17P + 0.1$

25

A few interesting things can be observed in the figure. First, line II indicates that there is a huge potential if a relevant EOR case can be found. Line III shows that such an integration project will be robust against significant added investments. Further, line IV

30   illustrates the point that even by passing half of the savings in the gas price over to the EOR operator, the net GTL gas price actually will be lower for a high gas price in the area. At a nominal gas price of 1 USD/MMbtu, the vertical arrows indicate that the added value for both plants is 1.085 USD/MMbtu of GTL feed gas.

There will be no incentive for a GTL/EOR integration at a nominal gas price below the crossing of lines I, III and IV, i.e. when $I = bcP$, or when the added investment equals the potential for nitrogen sales. This occurs for a gas price of I/bc, or 0.085 USD/MMbtu in this example. The only case where a negative gas price will encourage

5   integration is when the investment of integration is negative, a situation that may occur when there is no alternative use for the excess energy from the GTL plant.

Claims

1.

A method for increasing oil recovery from an oil reservoir in which method gas is
5   injected into the reservoir, comprising the steps of:
-    separation of air into an oxygen-rich fraction and a nitrogen-rich fraction,
-    providing a natural gas stream and leading the natural gas stream and at least a
     part of the oxygen-rich fraction to a reformer for conversion to synthesis gas
     mainly comprising H_2, CO, CO_2 and lower amounts of non-converted methane,
10   water vapor and nitrogen,
-    formation of methanol or other oxygenated hydrocarbons or higher
     hydrocarbons from the synthesis gas in a synthesis unit,
-    withdrawing raw synthesis products and a waste gas from the synthesis unit, and
-    injecting the nitrogen-rich fraction and at least a part of the waste gas into the oil
15   reservoir to increase the oil recovery from the reservoir,

2.

A method according to Claim 1, wherein all or some of the waste gas from the synthesis
unit is sent to a CO2 recovery unit including a CO shift converter where CO2 is
20   removed and injected into the reservoir and the remaining hydrogen-rich stream is used
for other purposes.

3.

Method according to claim 1 or 2, wherein steam or water generated during the syngas
25   production and/or synthesis is injected into the reservoir.

4.

A plant for providing gas for downhole injection for pressure support in an oil reservoir
for recovering of hydrocarbons and production of oxygenated hydrocarbons or higher
30   hydrocarbons from natural gas, comprising:
-    an air separation unit (2) for production of an oxygen-rich fraction for supply to
     processes that require oxygen, and a nitrogen-rich fraction for injection;

- a reformer (8) for conversion of a mixture of natural gas, water and oxygen or oxygen enriched air from the air separation unit into a synthesis gas comprising mainly H_2, CO, CO_2 and small amounts of methane in addition to any inert gas, such as nitrogen;

5 - a synthesis unit (15, 56) for conversion of the synthesis gas for synthesis of oxygenated hydrocarbons, or for synthesis of higher hydrocarbons;

- means for injecting gas (6) into the reservoir;

- means for transferring nitrogen from the air separation unit to the means for injecting gas; and

10 - means for transferring at least a part of a waste gas from the synthesis unit to the means for injecting gas.

5.

A plant according to Claim 4, additionally comprising a tail gas treatment unit (63) for
15 removing CO by a shift reaction and separation of hydrogen from the remaining tail gas.

6.

Plant according to claim 5, comprising means (65) for transferring the remaining tail gas from the tail gas treatment unit (63) to the means for injecting gas (6).

20

7.

Plant according to any of the claims 4 to 6 wherein the synthesis unit (15, 56) comprises one or more once-through Fischer-Tropsch units for synthesis of higher hydrocarbons.

25 8.

Plant according to claim 7, comprising means for introducing all or parts of the separated hydrogen from the tail gas treatment unit (63) into the Fischer-Tropsch loop to adjust the H_2/CO ratio to a desired level.
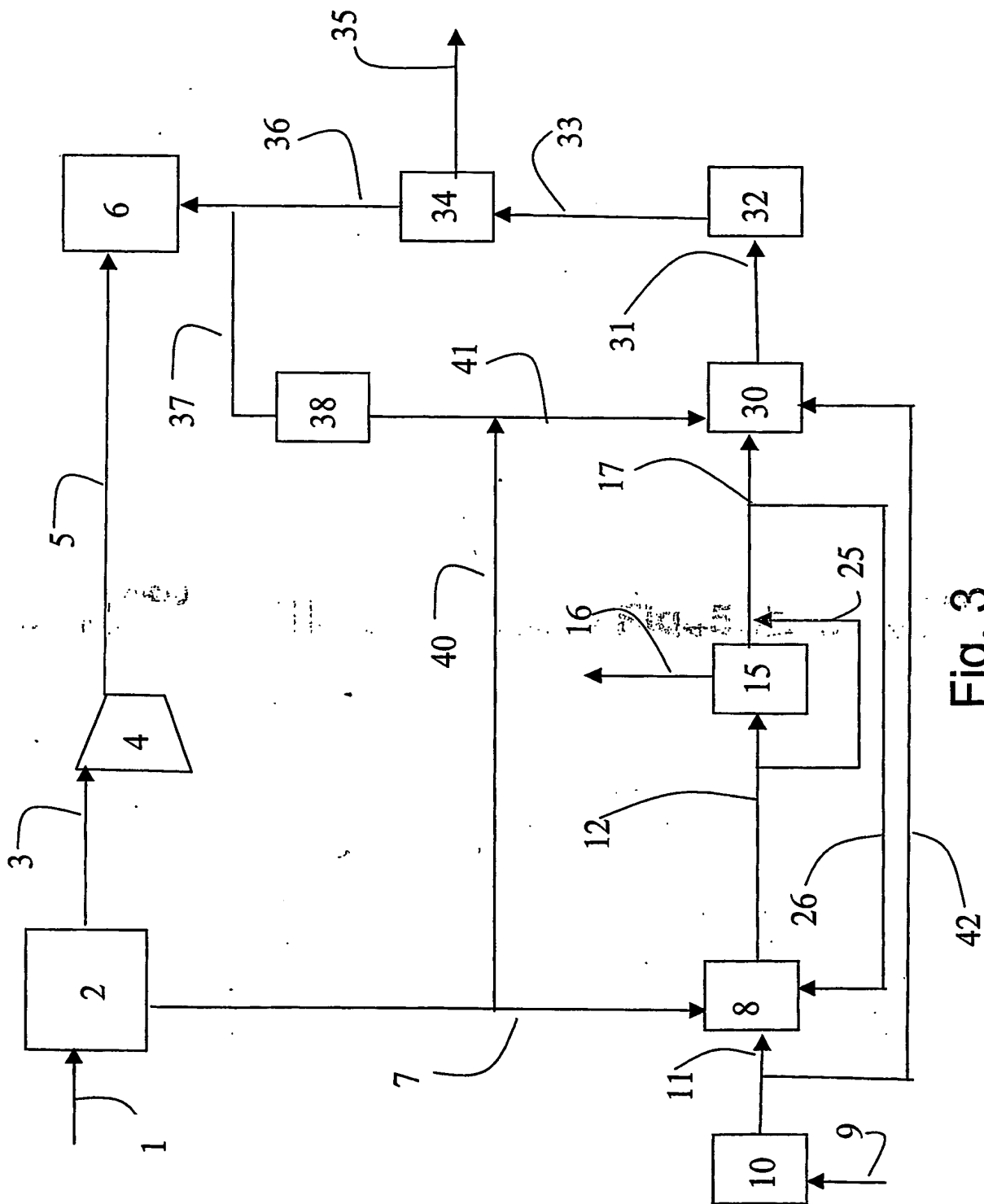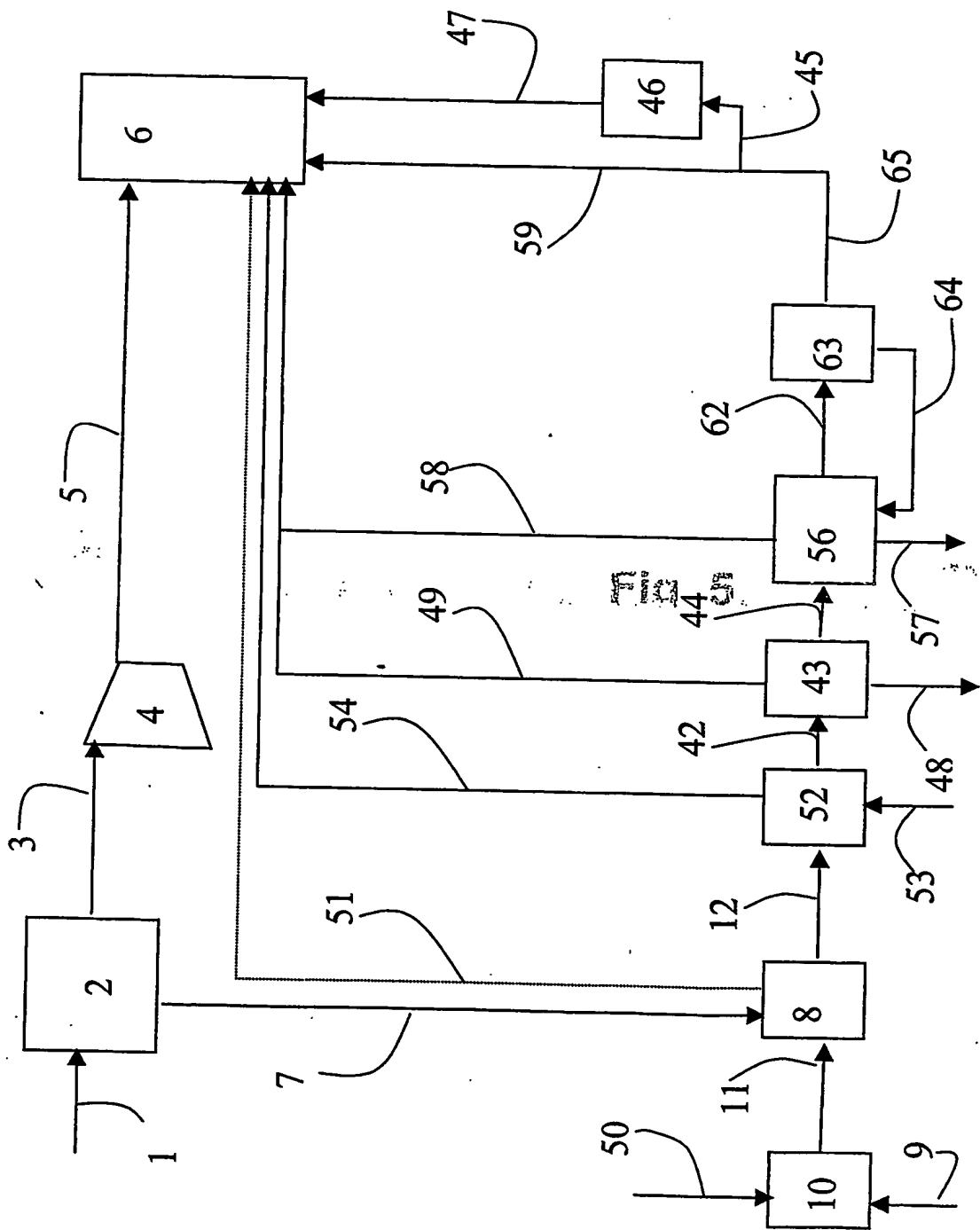
Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5